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AB INITIO POTENTIAL ENERGY CURVE FOR CH BOND DISSOCIATION IN METHANE

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Ab initio calculations on $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ were performed at the MP4/6-31G** level including all single, double triple and quadruple excitations. Although triple excitations have little effect on the dissociation energy, they are very important in the 2–3 Å range. The potential curve appears to rise more sharply than a Morse curve in this region. Correlation effects are not important for the HCH angle optimization.

1. Introduction

For most polyatomic molecules the details of bond rupture processes are not well defined, and the shape of the potential surface along the dissociation path is uncertain. Even for methane, a molecule which has attracted the attention of a number of investigators, this information remain unclear. Although rate constant measurements [1] for the reaction $\text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}$ have been made, they have not been successfully interpreted and understood in terms of transition state theory. Essential information necessary for the characterization of methane and its associated reactions is still lacking.

Determination of the methane potential energy surface is particularly important for answering several fundamental questions. Although $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ dissociation probably does not have a saddle point, when variational rate theory [2] is applied, the transition structure, and thus, the bimolecular and unimo-

lecular rate constants are expected to depend upon the shape of the potential energy surface. The vibrational energy levels of bound methane are strongly dependent on the potential energy surface. Also, the shape of the potential energy surface will determine whether classical trajectories are chaotic or quasiperiodic [3]. From the correspondence between classical and quantum mechanics [4], one expects the vibrational wavefunctions for chaotic quantizing trajectories to spread over the complete coordinate space, while the vibrational wavefunctions for quasiperiodic quantizing trajectories are expected to be localized in specific regions of the coordinate space. It has been suggested that such quasiperiodic trajectories may even extend into the quasi-continuum above dissociation [5].

This study has been initiated in an attempt to begin clarifying some of these issues. Since methane is the simplest of the alkane series, any comprehensive theoretical study of alkane decomposition and alkyl radical recombination processes ought to commence with an understanding of methane's properties and reactions. We focus here on the results of ab initio calculations of the methane potential energy surface,

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discussing both characteristics of the methane system and features of the perturbation technique used in the calculations.

2. Method

The ab initio calculations were carried out with the GAUSSIAN 80 series of programs using a polarization (6-31G**) basis set. This basis set is an extended basis of the split-valence type, augmented by six cartesian d orbitals on non-hydrogen atoms and three p orbitals on the hydrogen atoms. Energies were calculated at both the closed-shell restricted Hartree-Fock (RHF) and the open-shell unrestricted Hartree-Fock (UHF) level. Correlation effects were estimated by means of Møller-Plesset perturbation theory. The perturbation calculations were carried out through complete fourth order, i.e. the final fourth-order energies were computed in the space of single, double, triple and quadruple substitutions (MP4) with the perturbation theory applied to all the orbitals (valence and core) of the molecule.

The convergence properties [6] of the perturbation theory were investigated using Padé approximants [7]. This technique, which has been used effectively in previous studies [8,9], allows an estimate to be made of the contributions from the higher-order

terms of the perturbation series. The fourth-order (MP4) energy calculations were compared with the [2,1] Padé approximant, where

$$[2,1] = E_{\text{SCF}} + \frac{E_2}{1 - E_3/E_2 + E_3^2/E_2^2 - E_4/E_2}.$$

Two sets of geometries were used in the energy calculations. The first series of calculations was carried out by altering the length of a single C-H bond (symbolized by C-H*) while maintaining the remaining three C-H bonds at their equilibrium bond length (1.086 Å) and the HCH angles at the tetrahedral value. This process results in a pyramidal methyl radical at infinite extension of the C-H* bond. In the second series of calculations, the pyramidal angle (the angle formed by the C-H* bond and the unchanged C-H bonds) was optimized at each step along the dissociation path. Energy gradients were used to optimize at the SCF level; a three point parabolic fit was used for the MP4 optimization (step size = 1°).

3. Results

Table 1 presents a summary of the energy calculations as a function of the C-H* bond length with the angles fixed at the tetrahedral value. For C-H* bond lengths less than or equal to 1.5 Å, the re-

Table 1
Total energies for methane at various extensions of the C-H* bond a)

Bond length b)	Method	SCF	MP2	MP3	MP4SDQ c)	MP4
0.757	RHF	-40.057181	-40.225068	-40.243360	-40.245656	-40.248539
1.036	RHF	-40.200031	-40.368143	-40.386338	-40.388874	-40.392014
1.086	RHF	-40.201688	-40.369848	-40.388041	-40.390666	-40.393863
1.136	RHF	-40.200011	-40.368231	-40.386430	-40.389161	-40.392420
1.5	RHF	-40.142526	-40.312131	-40.330883	-40.335036	-40.338906
2.0	RHF	-40.046590	-40.223017	-40.244933	-40.253385	-40.258718
	UHF	-40.071391	-40.214243	-40.232437	-40.236746	-40.239416
2.25	RHF	-40.006513	-40.189244	-40.213964	-40.225811	-40.232252
2.5	RHF	-39.972162	-40.163248	-40.191644	-40.207922	-40.215835
	UHF	-40.056490	-40.191401	-40.208808	-40.211534	-40.213771
3.0	RHF	-39.918088	-40.132399	-40.171430	-40.200227	-40.212575
	UHF	-40.053480	-40.186962	-40.204310	-40.206846	-40.209004
∞	UHF	-40.052502	-40.185537	-40.202893	-40.205402	-40.207532

a) Energy in hartree; 1 hartree = 627.51 kcal/mol.

b) Remaining three CH bonds held constant at 1.086 Å; all HCH angles fixed at the tetrahedral value.

c) Fourth-order Møller-Plesset in the space of single, double and quadruple excitations.

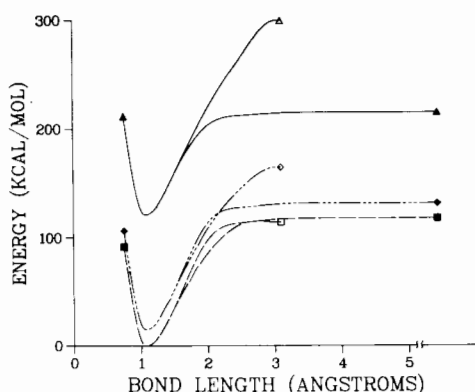


Fig. 1. CH_4 dissociation to CH_3 and H . Open symbols denote RHF calculations; solid symbols are UHF calculations; Δ , \blacktriangle and solid line for the HF level; \diamond , \blacklozenge and solid line for the MP2 level, \square , \blacksquare and short dashes for the MP4 level.

stricted (RHF) and unrestricted (UHF) wavefunctions are identical (the σ orbital of the $\text{C}-\text{H}^*$ bond is doubly occupied). In the region between 1.5 and 1.75 Å the RHF and UHF potential energy curves separate. The unrestricted calculations at 2.0, 2.5 and 3.0 Å, have both the σ and the σ^* orbitals of the $\text{C}-\text{H}^*$ bond singly occupied. Selected data from table 1 are presented graphically in fig. 1.

The above data support several observations. First, the single and triple substitutions appear to make substantial contributions to the energy calculation when the length of the $\text{C}-\text{H}^*$ bond is intermediate between equilibrium and infinite extension. However, the [2, 1] Padé approximant analysis indicates that the Møller–Plesset perturbation theory based on the RHF wavefunction converges very slowly when the $\text{C}-\text{H}^*$ bond length has reached 2.5 Å, and that the MP4 energy may not be an adequate estimate of the fully converged series (fig. 2). Consequently, while the inclusion of the single and triple substitutions does contribute to lowering the energy, the MP4 level of calculation is *not* sufficient to represent the methane potential energy surface properly in the intermediate region between 2.0 and 3.0 Å.

Secondly, the potential energy curve as a function of the $\text{C}-\text{H}^*$ bond length differs from the prediction of a Morse function. The energy curve and the corresponding Morse function are plotted in fig. 3 for the MP4 optimized geometries. Comparison of MP4 calculations with the [2,1] Padé approximant suggests

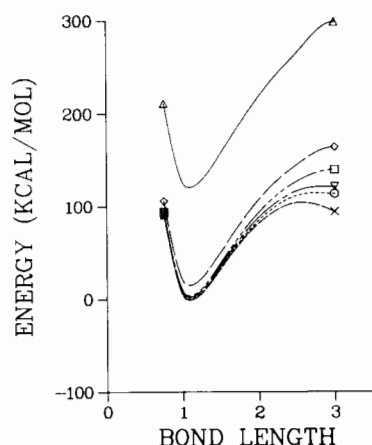


Fig. 2. Convergence of the restricted Møller–Plesset perturbation theory along the methane dissociation potential. Δ RHF, \diamond MP2, \square MP3, ∇ MP4SDQ, \circ MP4, \times Padé approximant. Bond length in Å.

that the actual dissociation curve for methane lies between the MP4 curve and the Morse curve, and probably does not contain a bend as sharp as the MP4 curve in the 2.0–3.0 Å region.

Finally, the variation of the optimized pyramidal angle as a function of the $\text{C}-\text{H}^*$ bond length is summarized in table 2 and plotted in fig. 4. It appears that electron correlation plays, at best, only a minor role in determining the optimized geometry of the CH_3 moiety as the $\text{C}-\text{H}^*$ bond ruptures.

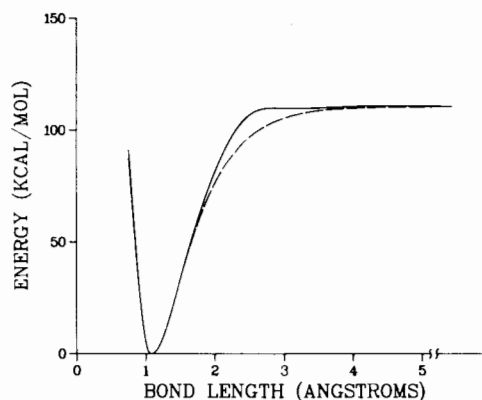


Fig. 3. Comparison of the Morse curve (dashed) with the MP4 calculations (solid) at the optimized HCH angles. The RHF data is used for distances less than or equal to 3.0 Å, and the UHF data for distances greater than 3.0 Å.

Table 2
Optimized bond angles and total energies along the dissociation path a)

SCF optimized			MP4 optimized	
bond length	angle	energy	angle	energy
0.757	111.08	-40.057548	111.33	-40.248933
1.086	109.47	-40.201688	109.46	-40.393846
1.5	105.89	-40.144047	105.71	-40.340360
2.0	100.57	-40.053872	100.57	-40.264690
2.5	96.29 a,b)	-39.985923	96.47	-40.224104
3.0	91.95 c)	-40.063239	91.30	-40.219059
∞	planar c)	-40.062322	planar	-40.217593

a) Energy reported in hartree, angles in deg. All calculations are restricted Hartree-Fock (RHF) unless otherwise noted.

b) UHF calculation gives 94.98. c) UHF values.

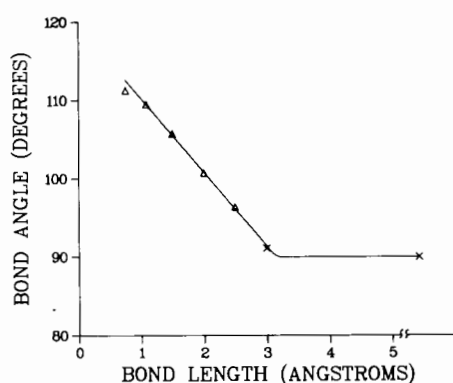


Fig. 4. Variation of the pyramidal angle as a function of bond length. Δ represents RHF calculations; \times represents UHF calculations.

4. Discussion

Measurements of the thermochemical properties of methane are available in the literature [10,11] and allow an estimate to be made of the depth of the methane potential well. These thermodynamic data, properly corrected to 0 K, yield a value of -112.45 kcal/mol for the well depth (D_e). In comparison, the value obtained from the ab initio calculations at the MP4 level for the optimized geometries is -110.60 kcal/mol, a difference of 1.85 kcal/mol between the calculated and experimental values. In their study of the CH_3OH system, Adams et al. [12] observed a similar error in the calculated dissociation energy. Using a double-zeta basis plus polarization functions for a calculation at the MP4 level, they found a discrepancy of 1–3 kcal/mol. The depth of the methane

potential well also has been calculated at the MP4 level using the 6-311G** basis (a triple-zeta basis plus polarization functions) yielding -109.44 kcal/mol [13] which differs from the present results by 1.16 kcal/mol.

At the Hartree-Fock level (SCF), the potential energy curves show no unexpected behavior. For the tetrahedral geometry, the well depth of -93.62 kcal/mol is 23.30 kcal/mol less than the MP4 value, and the RHF dissociation curve approaches the ionic limit. The UHF wavefunction separates from the RHF wavefunction in the region between 1.5 and 1.75 Å and proceeds to the correct limit. The calculations performed at the various levels of perturbation theory exhibit several noteworthy features. At 1.086 Å the triple substitutions lower the energy by 2.01 kcal/mol, and at infinite extension of the C-H* bond, they lower the energy by 1.34 kcal/mol relative to the MP4SDQ calculations. Since these two contributions are approximately the same size, the effect of the triple substitutions on the estimated depth of the potential well is minimal. In fact, the MP2 calculations estimate a well depth only 1.3 kcal/mol higher in energy than the significantly more difficult MP4 calculation. The [2,1] Padé approximant calculations for the RHF wavefunction in the region near equilibrium and for the UHF wavefunction at infinite extension of the C-H* bond, agree well with the MP4 calculations in these regions. Consequently, in these regions, we expect that the MP4 calculations properly represent the methane potential energy surface.

The situation is somewhat more complex in the intermediate region between 2.0 and 3.0 Å. As we

have noted above, the [2,1] Padé approximant analysis indicates that the Møller–Plesset calculations based on the RHF wavefunction may not be fully converged for C–H* bond lengths greater than 2.5 Å[‡]. This can be attributed to the importance of single excitations (e.g. $\sigma \rightarrow \sigma^*$) in the intermediate region [2]. Although single and triple substitutions contribute to lowering the energy relative to the MP4 calculations with only double and quadruple excitations (MP4DQ), their inclusion in a fourth-order perturbation calculation appears to be insufficient to produce an adequate representation of the methane potential energy surface in the intermediate region. We expect that the actual methane surface in the intermediate region lies somewhat below the current MP4 curve. In retrospect, the breakdown of Møller–Plesset theory in the intermediate region is not totally surprising since some of the energy denominators approach zero in this region. Rather than dwelling on the theory's limitations, it should be emphasized that the Møller–Plesset technique performs very well up to distances approaching twice the equilibrium bond length.

Since one of the primary motivations of this study was to determine the behavior of methane as it dissociates to methyl radical and hydrogen atom, we were particularly interested in determining the shape of the energy surface as a function of bond extension. In the past, many different functions [14] have been proposed as models for the diatomic oscillator, with the Morse [15] function ($V = D_e \{ 1 - \exp[-\beta(r - r_0)] \}^2$) emerging as the most commonly adopted representation. Our initial inclination was to expect that the dissociating methane molecule might behave as a complex diatom whose potential surface could be adequately described by a Morse function. While the Morse potential is indeed a good approximation in the region near equilibrium (fig. 3), the energy surface departs significantly from the Morse curve when the C–H* bond is extended between two and three times its equilibrium length. In this region, the *ab initio* calculations (MP4) indicate that the energy surface rises more steeply and bends more sharply than the standard Morse potential.

In order to test the behavior of the MP4 calculation relative to the Morse function, two additional studies were done. We first examined the H–F bond

[‡] The [2,1] Padé approximant calculations for the UHF wavefunction agree very closely with the MP4 calculation.

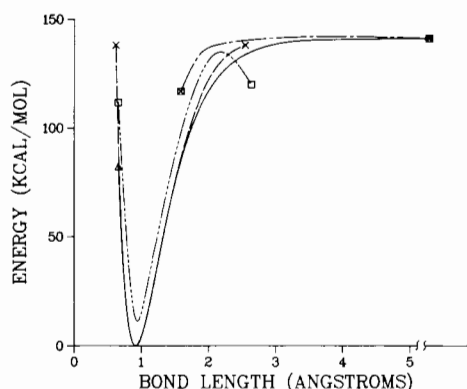


Fig. 5. Comparison of HF dissociation potentials; Morse curve, Δ and solid; RKR curve, \times and large dashes; RMP4 curve, \square and three short and one long dash; UMP4 curve, $*$ and one short and one long dash.

and compared our calculated results with an RKR [16–20] curve derived from experimental data. As fig. 5 illustrates, the restricted MP4 curve is parallel to the RKR curve up to a bond distance of ≈ 2.1 Å. The Morse curve lies below both the restricted MP4 and the experimental curve and rises less steeply than either of them. The [2,1] Padé approximant analysis exhibited close agreement with the restricted MP4 data up to a distance of 1.9 Å (more than twice the equilibrium bond length).

In the second study, the behavior of the MP4 calculations for the B–H bond was investigated. Since an RKR curve based on experimental data for BH is not available, the MP4 calculations were compared to GVB computations of Harding [21]. The GVB calculations were carried out with a double-zeta basis plus polarization functions and included all single and double excitations from the two reference determinants (GVB + 1 + 2). Utilizing the restricted MP4 data of Kvasnička [22] and our unrestricted MP4 calculations we find that the restricted MP4 curve begins to diverge markedly from the GVB + 1 + 2 curve at a distance of ≈ 1.7 times the equilibrium bond length. The [2,1] approximants agree very well with the qualitative behavior of the GVB + 1 + 2 curve up to a distance of 2.2 Å (≈ 1.8 times the equilibrium bond length).

These investigations of the H–F, B–H, and C–H bonds reinforce our earlier observation that MP4 calculations are *not* sufficient to represent the methane potential energy surface in the intermediate region. The [2,1] Padé approximant analysis exhibited the

closest agreement with the MP4 calculation in the case of the H–F bond and poorest agreement in the case of the B–H bond. The results for the C–H bond lie between these two extremes. Consequently, we expect the actual methane potential curve to lie between the MP4 curve and the Morse curve, bending less sharply than the MP4 curve in the intermediate region.

Finally, as one of the bonds in methane is extended, the molecule undergoes a pronounced transformation of its angular geometry, changing from a tetrahedral structure to a planar methyl radical and a free hydrogen atom. In examining the angular variation several features are apparent.

As the data in table 2 demonstrate, correlation effects contribute very little to the change in angular geometry. The SCF-optimized value of the angle is only slightly altered when the angular geometry is optimized at the MP4 level. Secondly, the variation of the angle as a function of the C–H* bond length is linear over the region from 1.086 to 3.0 Å, as depicted in fig. 4. Only after the C–H* bond has been extended over 2.5 times its equilibrium length does the angle change more slowly and asymptotically approach the planar value. The observed abrupt change in the angle could be due to the limited radial extent of our basis set. To investigate this possibility, we re-optimized the angular geometry at 3.0 Å in a UHF calculation at the SCF level using the 6-31G** basis set augmented with a diffuse SP shell (exponent = 0.044) on the carbon atom. Since the re-optimized angle, 91.1°, does not differ significantly from the previous value, the abrupt change in the angle as a function of bond length (fig. 4) does not appear to be an artifact of our basis set.

It should also be observed that the MP4 energy along the dissociation path and the angle do not assume their asymptotic forms simultaneously. The energy surface executes its sharpest bend when the C–H* bond has been extended to a length of ≈ 2.5 Å, while the angular geometry remains virtually a linear function of bond length until this bond has reached a length of 3.0 Å. Since we expect the actual methane surface to lie between the MP4 curve and the Morse curve, this contrast may not be as stark as is indicated here.

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